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I. A. Arbuzova, V. N. Efremova, and I. K. Ulezlo

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Abstract

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CHEMISTRY

I. A. Arbuzova, V. N. Efremova, and I. K. Ulezlo

ON POLYMERIZATION IN VISCOUS MEDIA

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A distinctive feature of polymerization reactions is the large effect of the surrounding medium on the rate of polymer-chain termination.

Various factors that retard the termination reaction increase both the polymerization rate and the length of the polymer chains. From this point of view, a large change in the viscosity of the monomer, which occurs during bulk polymerization, should influence the polymerization process. In the initial period most polymerization reactions proceed at a constant rate. If, however, polymers with high molecular weight are formed and the viscosity of the system rapidly increases, the reaction rate also begins to increase. Simultaneously with the increase in the reaction rate, the molecular weight of the polymer increases. In accordance with this proposition, Trommsdorff (^1) found that if the viscosity of methyl methacrylate is increased by dissolving cellulose propionate, the polymerization rate increases. In contrast to the indicated effect, the influence of inert solvents that lower the viscosity of the reaction medium is manifested in a decrease in the rate of the polymerization reaction and in a decrease in the molecular weight of the polymer, proportional to the decrease in monomer concentration (^2). Most solvents, by interacting with the polymer chain, cause chain termination or chain transfer, as a result of which the polymerization rate decreases in accordance with dilution, while at the same time the molecular weight of the polymer falls more rapidly than can be explained by dilution (^3). S. S. Medvedev (^4), in studying the polymerization of vinyl acetate in benzene and of styrene in carbon tetrachloride, showed that under these conditions chain termination occurred as a result of interaction of the growing chains with the solvent.

The opposite effect is observed when polymerization is carried out in a medium that dissolves the monomer and is not a solvent for the polymer. Thus Norrish and Smith (^5) showed that methyl methacrylate polymerizes more rapidly in solvents that cause precipitation of the polymer than in good solvents for both the monomer and the polymer. Similar results were obtained by Hevord (^6) in the polymerization of isopropenyl ketone. In both cases the increase in the polymerization rate was accompanied by an increase in the intrinsic viscosity of the polymer formed. Melville (˜7), in studying the polymerization of vinyl acetate in *n*-hexane, which is not a solvent for the polymer, found that as the reaction proceeded its rate increased. Along with this, the value of the rate constant for chain termination decreased. Thus, the literature has covered the question of the influence on the polymerization process of solvents that dissolve the monomer and the polymer, as well as of monomer solvents that are not solvents for the polymer. The question of the influence of the viscosity of the solvent has not been discussed in the literature. Meanwhile, it should be expected that the viscosity of the solvent must influence the polymerization rate and the properties of the polymer formed.

The present communication is devoted to the question of the polymerization of acrylamide, methacrylamide, and methylolmethacrylamide when glycerin is used for the first time as a solvent. All the indicated monomers and their polymers are soluble in glycerin, forming highly viscous solutions. The literature data on the polymerization of the above-mentioned monomers concern the study of polymerization in low-viscosity solvents.

Thus, Schulz, Renner, et al. ([8]) studied the radical polymerization of acrylamide in solvents—water, methyl alcohol, and aqueous-alcohol mixtures.

Polymers of methacrylamide were obtained by Arcus ([9]) in the polymerization of methacrylamide in toluene and ethyl acetate in the presence of 2.5-5% benzoyl peroxide, and by Pinner ([10]) in polymerization in an aqueous medium. On the polymerization of methylolmethacrylamide there are only the indications of Feuer and Lynch ([11]), according to whose data methylolmethacrylamide polymerizes in an aqueous medium in the presence of acids, and also in organic solvents in the presence of ionic catalysts, with formation of an insoluble polymer.

The experiments carried out showed that acrylamide, methacrylamide, and methylolmethacrylamide readily polymerize in glycerin under the action of ultraviolet irradiation, with formation of polymers of high viscosity.

Starting materials and method of investigation

Acrylamide was obtained by partial saponification of acrylonitrile ([12]). The crude product was purified by threefold recrystallization from benzene; after drying in a vacuum desiccator over paraffin shavings, m.p. 85°, N 19.70%; calculated for C_3H_5ON: N 19.71%.

Methacrylamide was obtained by the method of Arcus ([9]), by the reaction of methyl methacrylate with aqueous ammonia. After recrystallization from alcohol it had a melting point of 111°. The content of methacrylamide (determined by the bromination method) was 99.77%.

Methylolmethacrylamide was synthesized by the method of Feuer and Lynch ([11]), by the reaction of methacrylamide with paraformaldehyde in carbon tetrachloride medium. The crude product was recrystallized from ethyl acetate. After drying in a vacuum desiccator, m.p. 53.5–54.5°, N 12.12%; calculated for C_5H_9ON: N 12.17%.

Glycerin was purified by distillation under vacuum. For the experiments, a fraction with b.p. 167° (5 mm), $d_4^{15} = 1.2642$, $\eta_{20} = 1431$ cP was used.

Before the polymerization was carried out, water was purified by distillation over potassium permanganate in a stream of nitrogen free of oxygen.

To study the influence of the viscosity of the solvent on the rate of polymerization and the properties of the polymer, polymerization was carried out in two solvents: water and glycerin, whose viscosity at room temperature exceeds the viscosity of water by \$ \$1400 times. Polymerization was carried out under the action of ultraviolet irradiation*.

A PRK-2 lamp served as the light source. For the study of polymerization, the region $\lambda = 3000$ Å was used. Polymerization was carried out in sealed ampoules made of Pyrex glass. At the end of the process the polymers were purified by precipitating aqueous solutions with methyl alcohol, followed by repeated reprecipitation. In polymerization experiments in glycerin medium, the contents of the ampoules were first dissolved in water, and then the aqueous-glycerin mixture containing the polymer was precipitated with methyl alcohol. Further purification was carried out by dissolving the polymer in water, followed by precipitation with methyl alcohol.

The viscosity of the polymers was determined in an Ostwald viscometer, and the viscosity of glycerin in a Hoppler viscometer. The tables give the characteristic viscosities of the polymers; the viscosity of glycerin was taken in centipoises.

The results of experiments on the polymerization of acrylamide are given in Table 1. From the data of Table 1 it is evident that, upon irradiation of an aqueous solution of acrylamide at a temperature of 40° for 42 h, the polymerization reaction did not occur; after irradiation of the acrylamide solution in glycerin for 12 h, conversion reached 87.5%. With increasing monomer concentration, the reaction rate and the characteristic viscosity of the polymer increase. With a lowering of the reaction temperature, the characteristic viscosity of the polymers increases. The question of the reaction rate upon lowering the temperature will be discussed in the next communication.

Table 1

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* The polymerization of methylolmethacrylamide in an aqueous medium was also carried out in the presence of the initiator hydrogen peroxide.

Solvent	Acrylamide concentration, mol/l	Reaction temperature, °C	Reaction duration, min	Reacted, %	Reacted, mol.	Average rate, mol/l sec · 10^5	$[\eta]$
Water	1.58	40	2880	Not polymerized	Not polymerized	Not polymerized	Not polymerized
Glycerin	1.58	40	1020	87.5	1.3809	0.225	0.50
»	2.85	40	1020	98.48	2.7960	0.456	0.816
»	1.408	1	140	16.3	0.229	0.270	1.068
»	1.408	1	190	95.1	1.339	1.174	1.035
»	2.85	1	40	83.2	2.371	9.88	1.614

Table 2

Solvent	Methacrylamide concentration, mol/l	Reaction temperature, °C	Reaction duration, min	Reacted, %	Reacted, mol.	Average rate, mol/l sec · 10^4	Note
Water	1.176	19	1320	Not polymerized	Not polymerized	Not polymerized	
Glycerin	1.176	19	50	98.3	1.156	3.510	Insoluble
Same	0.62	19	60	66.7	0.413	1.165	Same

The results of some experiments on the polymerization of methacrylamide are given in Table 2. They indicate the high activity of the process of polymerization of methacrylamide in the presence of the solvent—glycerin.

The results of some experiments on the polymerization of methylolmethacrylamide in an aqueous medium are given in Table 3.

Table 3

Solvent	Methylolmethacrylamide concentration, mol/l	H_2O_2 concentration, mol/l	Reaction temperature, °C	Reaction duration, min	Reacted, %	Reacted, mol.	Rate, mol/l/sec $\cdot 10^6$	$[\eta]$
Water	0.782	0.072	40	2520	100	0.78	–	0.05
»	0.782	0.0375	35	1080	100	0.78	–	0.24
»	0.82	–	35	1335	57.7	0.45	0.563	0.85
»	1.44	–	35	615	20	0.288	0.78	1.41
»	1.74	–	35–40	130	12.4	0.216	2.76	2.15

From the data of Table 3 it is evident that, in the polymerization of methylolmethacrylamide in an aqueous medium in the presence of the initiator hydrogen peroxide and with simultaneous exposure to ultraviolet light, low-viscosity polymers are obtained. When polymerization is carried out under the action of ultraviolet irradiation, the characteristic viscosity of the polymer increases. Increasing the monomer concentration increases the rate of polymerization and the viscosity of the polymers.

Table 4 gives the results of some experiments on the polymerization of methylenemethacrylamide in glycerin medium.

The polymerization experiments carried out with acryl-, methacryl-, and methylenemethacrylamide indicate the influence of the viscosity of the solvent on the rate of polymerization and the molecular weight of the polymers.

Table 4

Solvent	Concentration of methylenemethacrylamide, mol/l	Reaction temperature, °C	Reaction duration, min	Reacted, %	Reacted, mol	Rate, mol/l/sec $\cdot 10^4$	$[\eta]$
Glycerin	0.87	20	30	31.2	0.271	1.5	2.75
»	0.457	20	60	84.4	0.386	1.068	1.94
»	0.457	16	50	44.5	0.203	0.565	2.63
»	0.235	20	150	52.8	0.124	0.138	–

From a comparison of the results obtained in the polymerization of methylenemethacrylamide in aqueous solution and in glycerin medium, it follows that the rate of polymerization in glycerin medium many times exceeds the rate of polymerization in aqueous medium. The intrinsic viscosity of the polymers is also higher in the case of glycerin. Polymerization in glycerin medium makes it

Fig. 1. Influence of temperature on the viscosity of glycerin

Figure 1: Fig. 1. Influence of temperature on the viscosity of glycerin

possible to show the influence of changes in the viscosity of the medium on the properties of the polymers without changing the nature of the solvent. When the polymerization temperature of acrylamide was lowered from +40° to +1°, the viscosity of the polymers formed increased approximately twofold (see, for example, experiments 3 and 6 in Table 1).

Figure 1 gives the curve of the change in the viscosity of glycerin as a function of temperature, compiled on the basis of literature data (^{13}). From the curve it is evident that the viscosity of glycerin at 1° is 11000 cP, and at 40° is ~ 500 cP. Thus, changing the reaction temperature from 40 to 1° changes the initial viscosity of the reaction medium by approximately a factor of 20, which causes a large slowing of the diffusion rate of the growing polymer chains and a further decrease in the termination rate, and also leads to an increase in molecular weight.

Fig. 1. Influence of temperature on the viscosity of glycerin

Institute of High-Molecular Compounds
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.